



(11) Publication number : **0 489 585 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number : **91311287.6**

(51) Int. Cl.⁵ : **C07C 6/04, B01J 23/30**

(22) Date of filing : **04.12.91**

(30) Priority : **05.12.90 FI 906020**

(43) Date of publication of application :
10.06.92 Bulletin 92/24

(84) Designated Contracting States :
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

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(54) **A metathesis process for olefines and a catalyst to be applied therein.**

(57) A metathesis process for the conversion of olefines, in which an olefine is brought into contact with a solid catalyst system comprising, on a solid silica carrier, 0.1 - 40% by weight of a wolfram compound, under reaction conditions in which the catalyst system converts the olefine into olefines having a different molecular weight; the silica carrier being a magnesium oxide or titanium oxide-containing co-gel prepared by means of a co-gelling system.

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The invention relates to a metathesis process for the conversion of olefines as well to a catalyst to be applied therein.

The metathesis or disproportionation of olefines refers to a reaction, in which one or more olefines are converted into olefines having a different molecular weight. The olefine may be disproportionated with itself into olefines having a higher molecular weight and into olefines having a lower molecular weight. In this case, the reaction may be called a "self-disproportionation". Two different olefines can also be converted into other olefines by means of the metathesis reaction.

In order to function, the metathesis reactions of olefines require a catalyst system, which includes a transition metal compound, often a cocatalyst, and sometimes also a compound acting as a promoter. Catalyst systems based on wolfram and molybdenum are especially efficient. Such catalysts generally comprise a wolfram or molybdenum oxide on an inorganic carrier, such as silica or alumina. It is known to add to such catalysts different substances acting as a promoter. Thus, for example according to the EP publication 152 112, a titanium oxide or titanium-containing substances are added to the surface of the catalyst as a promoter. The US patent 4559320 describes the use of a wolfram catalyst on a silica carrier, to which catalyst is also added a magnesium oxide.

In accordance with the present invention, it has surprisingly been observed that the activity of said wolfram catalysts can be that contain magnesium oxide or titanium oxide considerably improved in the metathesis process of olefines, if a silica co-gel is used as a carrier, in which the silica is gelled together with a magnesium oxide or titanium oxide before the addition of wolfram. Thus, the inventive metathesis process is characterized by the characteristic features presented in Claim 1.

In accordance to a certain additional feature of the invention, improvements are also achieved in the activity, if the catalyst in the metathesis process of olefines is fitted into a reactor in a certain manner.

In the catalyst to be used in the inventive process, the co-gel to be used as a carrier may be prepared from solutions of silicate and magnesium or titanium compounds. The sodium silicate solution is thus reacted with a suitable magnesium salt, e.g. with a magnesium oxide, magnesium hydroxide, magnesium nitrate, magnesium sulphate, magnesium acetate) the pH-value being over 8, whereby co-gels are obtained, whose general properties depend on the SiO_2/Mg stoichiometry and the processing conditions. The magnesium salts may alternatively be mixed with hydrosols, which have been obtained by acidating sodium silicate solutions when the pH-value is less than 4, whereby silica/magnesia co-gels are obtained, whose general properties depend on the stoichiometric conditions used, the pH-value, the reaction time and the temperature. The testing and adjustment of these parameters is apparent to those skilled in the art. The hydrogel obtained in this way is washed and dried. Silica-titanium oxide co-gels are prepared in a similar manner.

The co-gels obtained are advantageously ion exchanged by means of any acid or ammonium salt for removing the alkali metal cations suitable for the ion exchange. In addition, the co-gels obtained can be activated before use by heating them to a temperature of over 200°C into a water content of about 10%, whereby at least the surface layer of the co-gel changes into an acid form.

In the inventive process, such co-gels can be preferably used as a carrier of the catalyst, in which the Si/Mg ratio is in the range 10/1 - 10000/1 or the Si/Ti ratio is in the range 10/1 - 10000/1.

The wolfram catalyst to be used in the inventive process is prepared from co-gels prepared in the manner described above by adding thereto a wolfram oxide in any manner desired. The wolfram may be added either directly as an oxide or as precursor. In the last-mentioned case, the oxide precursor is changed into an oxide form by calcination. Suitable oxides or precursors are wolfram compounds, which can be changed into an oxide form in the calcination conditions. Examples of suitable wolfram compounds include oxides, halides, sulphides, sulphates, nitrates, acetates and their mixtures.

Examples of suitable wolfram compounds thus include wolfram pentachloride, wolfram dichloride, wolfram tetrachloride, wolfram hexafluoride, wolfram trioxide, wolfram dioxychloride, wolfram trisulphide, metawolfram acid, ortho-wolfram acid, ammonium phosphowolframite and ammonium metawolframite.

The quantity of the wolfram oxide or wolfram precursor in the co-gel carrier may vary from 0.1% by weight of wolfram oxide to 40% by weight. A suitable quantity is generally with the range 2-20% by weight.

The wolfram oxide or precursor may be added to the co-gel carrier either by dry mixing or by absorbing from a solution. In the latter case, the co-gel carrier is treated with a wolfram-compound solution, and the extra solution is then removed. Alternatively, the solution can be used only to such an extent, which the co-gel carrier is capable of absorbing.

If the wolfram compound is in the precursor form, a calcination is performed for the catalyst, in which it is heated in the presence of an oxygen-containing gas, e.g. air. The temperature required is generally 300-800°C and the reaction time from 15 minutes to 20 hours. The calcination can also occur in the presence of an olefine containing 2-20 carbon atoms.

A solid wolfram catalyst can be in the desired form, such as in the form of balls, granules or agglomerates,

when a solid-bed catalyst is used in the metathesis of olefines. If slurry catalyst systems are used, the catalyst is preferably in the form of a fine powder.

The inventive WO_3/SiO_2 metathesis catalysts can be applied to the metathesis reactions of olefines in a known manner. The metathesis reaction of olefines is typically performed within a temperature range of 250-500°C, preferably within the range of 380-430°C. The metathesis reaction is specific for the catalyst system used. A suitable temperature range for the WO_3/SiO_2 system is thus within the range of 300-450°C.

The metathesis is performed by bringing the feeding olefine in either a liquid or gas phase into contact with the inventive catalyst. If the reaction is performed in a liquid phase, suitable solvents or diluents may be used, such as saturated aliphatic hydrocarbons, e.g. pentane, hexane, cyclohexane, etc., or aromatic hydrocarbons, such as benzene or toluene. If the reaction is performed in a gas phase, suitable diluents may be used, such as aliphatic hydrocarbons, e.g. methane, ethane, propane, butane or inert gases, such as nitrogen.

The reaction time is not critical, and it may vary within a wide range. A reaction time from 0.1 seconds to 24 hours is generally sufficient.

The metathesis reaction is typically performed by passing the olefine through a reaction vessel, which is partially or totally packed full with the catalyst. It has been observed according to the invention that the activity and conversion of the catalysts can be essentially improved by diluting the wolfram-containing catalyst with such a carrier, which contains no wolfram. This may result from the fact that the reaction balance is reached very rapidly in the metathesis reaction. The reaction balance is reached in the catalyst already on its surface layers, whereby the remaining portion of the catalyst can no longer affect the balance position, but is in a way unnecessary. A considerably diluted catalyst can thus be used in the catalyst bed. Thus, in the inventive process, a catalyst bed can be used, which includes a catalyst containing ca. 6% of wolfram, the remaining portion being formed of the inventive carrier prepared by gelling.

The dilution in the catalyst bed can also be achieved so that the wolfram containing catalyst is placed under the carrier layers containing no wolfram or between such layers. The inert layer then acts as a heat compensator and a mixing intensifier.

In the inventive metathesis process there may be converted e.g. acyclic mono-olefines, e.g. 1-butene, 2-butene, 1-pentene, 2-pentene, 1-hexane, 1,4-hexadiene, 2-heptane, 1-octane, 2-nonene, 1-dodecene, etc. Propene is especially suitable. In addition thereto, a raffinate to be derived from an MTBE unit may be used as a feed, which raffinate contains various quantities of suitable butenes as well as paraffins acting as diluents. The oxygen containing components have to be removed before the metathesis reaction since they impede the reaction. For example an activated alumina a copper catalyst and molecular sieves can be used for purifying the raffinate feed.

Example 1

A metathesis catalyst was prepared by impregnating 1.34 g of a carrier (manufacturer Grace Co) twice with a 4% NH_4WO_3 water solution and by drying the water periodically by heating in an oven at 115°C. This silica titania co-gel is a silica titania carrier prepared by gelling, in which the titane is homogenously distributed into the whole gel quantity. The gel's titane content was 4.3%, particle size 0.05 mm surface area 467 m^2/g and pore volume 1.07 ml/g. The catalyst thus obtained was dried at 120°C overnight. The catalyst was examined in the propene metathesis reaction by loading into a tube reactor a mixture, which contained 0.102 g of the catalyst prepared in the manner described above and 0.718 g of the same carrier without wolfram. The catalyst was activated by passing through the catalyst bed first air at 600°C at a flow rate of 10 l/h for 1.5 hours and then nitrogen at the same temperature at a flow rate of 10 l/h for 30 minutes.

Thereafter, propene was passed into the reactor at 400°C first at a flow rate of 1.07 l/h and after 3 hours at a flow rate of 3.5 l/h. The propene then converted into ethene and butanes. The results are shown in Table 1, in which the activities of the catalyst are given as units g of the converted propene / g of $\text{WO}_3 \times \text{h}$. The percentages of the product distributions are percents by weight.

Table 1

Time (h)	Ethene (%)	Propene (%)	Butenes (%)	Others (%)	Conversion (%)	Activity (g/gh)
0	10.077	65.021	22.059	2.84	34.98	300.80
5	11.195	61.660	25.598	1.55	38.34	1078.80
10	11.104	61.871	25.649	1.47	38.13	1072.54
20	10.529	63.550	24.726	1.20	36.45	1025.32
30	9.957	65.445	23.584	1.00	34.56	972.01
40	9.729	66.165	23.198	0.91	33.83	951.76

The metal content of the catalyst was 5.25%.

The reaction was an extremely pure metathesis reaction without acid catalytic side reactions.

Example 2

A metathesis catalyst was prepared, as described in Example 1, but as a carrier was used a silica-magnesia co-gel (manufacturer W.R. Grace), which is a silica-magnesia prepared by gelling, in which the magnesium occurs only as surface ions. The gel's magnesium content was 1.0%, particle size 0.05 mm, surface area 334 m²/g and pore volume 1.07 ml/g. The catalyst obtained was examined in the propene metathesis reaction by loading into a tube reactor uppermost 0.0945 g of a pure catalyst and under this layer a mixture, which contained 0.0268 g of the catalyst prepared in the manner described above as well as 0.0707 g of a pure carrier. The wolfram content of the catalyst was 5.8% of the catalyst. The activation of the catalyst was performed as in Example 1.

Thereafter, propene was passed into the reactor at 400°C first at a flow rate of 3.0 l/h and after 2 hours at a flow rate of 5.0 l/h. The results are shown in Table 2.

Table 2

Time (h)	Ethene (%)	Propene (%)	Butenes (%)	Others (%)	Conversion (%)	Activity (g/gh) ²
0	9.921	48.985	34.597	6,50	51.02	1357.01
2	8.699	48.857	35.499	6.95	51.14	2267.36
5	9.468	51.393	37.294	1.85	48.61	2154.93
10	8.868	52.600	37.460	1.07	47.40	2101.42
20	7.797	58.856	33.053	0.29	41.14	1824.07

As in Example 1, the reaction was an extremely pure metathesis reaction without acid catalytic side reactions.

Reference example 1

A catalyst was prepared in the same way as described in Example 1, but a pure silica was used as a carrier. The wolfram content of the catalyst was 5.8% and 0.3782 g of this catalyst was used in the catalyst bed. The activation was performed by passing through the bed air at 600°C for 90 minutes.

The metathesis reaction of propene was examined in the presence of this catalyst according to Example 1. The results are shown in Table 3.

Table 3

	Time (h)	Ethene (%)	Propene (%)	Butenes (%)	Others (%)	Conversion (%)	Activity (g/gh)
5							
10	1	7.877	46.435	34.533	11.155	53.565	33.71*
	20	7.860	50.782	39.982	1.376	49.218	93.85**
	25	8.101	51.418	39.366	1.115	48.582	123.52***
15	29	7.407	54.803	36.863	0.927	45.197	173.50****

20 Note! The propene flows:

* 1.0 l/h

** 3.03 l/h

25 *** 4.04 l/h

**** 6.1 l/h

30 Comparison example 2

A metathesis catalyst was prepared, as described in Example 1, but PQ's silica CS-1231 was used as a carrier. Particle size of the silica was 0.6-1.6 mm and the surface area 330 m²/g. The carrier was impregnated twice with a 4% NH₄WO₃ water solution. After the drying, the catalyst was still sieved with an 0.5 mm sieve and the fine portion was rejected. The W content of the coarse portion used as catalyst was 5.8%.

35 MgO sieved with an 0.5 mm sieve and comprising 1.5% of the weight was mixed mechanically into the catalyst described above and packed by layers into the reactor such that 0.1064 g of the carrier and 0.1025 g of the catalyst were placed first and finally 0.1026 g of the carrier.

40 The activation of the catalyst was performed as in Example 1. The results are shown in Table 4.

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Table 4

Time (h)	Ethene (%)	Propene (%)	Butenes (%)	Others (%)	Conversion (%)	Activity (g/gh)
1	10.06	44.81	31.39	13.19	55.19	135.98*
3	9.35	48.19	34.52	7.86	51.81	370.78**
10	8.44	51.35	37.06	3.06	48.65	348.17
23	5.63	68.20	25.92	0.24	31.80	378.29***

Note! The propene feeds:

* 1.05 l/h

** 3.05 l/h

*** 5.07 l/h

Example 3

As in Example 1, a wolfram catalyst was prepared for an SiO_2 -MgO carrier in this example, the metal content of which catalyst was 6.03%. In the Example, a larger reactor was used, into which a larger quantity of the catalyst could be loaded, and ethene and t-and c-butenes were now used as feeds. The feeding ratios could be adjusted within a relatively large range for examining the properties of the catalyst. When loading the catalyst, an inert silicon carbide was now used as a diluent instead of a pure carrier. Starting from the top portion of the reactor, 1.0 g of SiC, 0.5 g of the catalyst and 5.06 g of SiC were packed into the reactor. The catalyst was calcinated, as in Example 1. Table 5 shows the results of the run. The temperature of the reactor was maintained at 400°C during the entire run.

Table 5

	Time (h)	Ethene (%)	Propene (%)	t-butene (%)	c-butene (%)	Others (%)	Met.act. (g/gmet*h)	Conversion (g/gh)
5	5	16.06	30.00	32.79	8.59	9.55	278.0	35.50*
10	60	13.10	51.31	21.10	12.74	0.61	475.5	49.17*
	125	14.74	48.12	23.33	12.29	0.51	445.9	46.78**
15	190	11.79	50.85	18.41	17.36	0.59	471.2	46.46**
	370	12.89	46.54	17.34	22.35	0.22	418.3	40.19***
	406	13.09	44.83	16.75	24.51	0.82	403.0	38.96***

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Note! The Table uses standard-run values, whereto it has been returned after each change.

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Feeds:

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* ethene 7.60 and t-butene 8.2 l/h

** ethene 7.60 and c-butene 8.2 l/h

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*** ethene 7.69 and c-butene 7.8 l/h

Example 4

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The Example was performed according to Example 3, and also the catalyst load was similar. As a feed was now used Neste's own raffinate (OLEFJK), which according to the product specification contains ca 50% of butenes and 8% of 1-butene, which are metathesis active. For removing the impurities, MeOH, MTBE, dimethyl ether and isobutene, in the olefine fraction, the feed was provided with an efficient purification system.

In this connection, also the reactor temperature was varied.

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Table 6

Time (h)	Ethene (%)	Propene (%)	t-butene (%)	c-butene (%)	Others (%)	Met.act. (g/gmet*h)	Conversion (g/gh)
4.5*	51.41	13.43	8.40	3.35	0.00	151.1	26.30
65.5	46.74	28.54	2.40	1.26	0.40	320.9	64.51
223.5	46.43	30.92	2.30	1.37	0.44	347.7	63.83

Note! The Table shows only a standard-level stability after the changes. The catalyst is extremely stable and requires no regeneration.

Feeds: ethene 17.66 l/h and raff II 7.24 l/h.

Claims

1. A metathesis process for the conversion of olefines, in which an olefine is brought into contact with a solid catalyst system comprising, on a solid silica carrier, 0.1-40% by weight of a wolfram compound, under reaction conditions in which said catalyst system converts the olefine into olefines having a different molecular weight, characterized in that the silica carrier is a magnesium oxide or titanium oxide-containing co-gel prepared by means of a co-gelling system.
2. A process according to claim 1, characterized in that the carrier contains at least 80% of silica and not more than 20% of magnesium oxide.
3. A process according to claim 1, characterized in that the carrier contains at least 80% of silica and not more than 20% of titanium oxide.
4. A process according to any of the preceding claims, characterized in that the catalyst system comprises a catalyst bed, which contains a mixture of the silica carrier, which does not contain wolfram or, optionally, another inert medium, such as silicon carbide, together with the wolfram-containing carrier.
5. A process according to any of the preceding claims, characterized in that the catalyst system comprises a catalyst bed, in which, in the direction of the feed flow, the first layer comprises the silica carrier, which does not contain wolfram, or, optionally, another inert medium, and the second layer comprises the wolfram-containing carrier.
6. A process according to any of the preceding claims, characterized in that the olefine comprises one or more olefines containing 2-20 carbon atoms.
7. A process according to claim 6, characterized in that the olefine mixture can contain 0-80% of i- or n-paraffins.
8. A process according to any of the preceding claims, characterized in that the metathesis reaction is per-

formed at a temperature of 380-430°C and at a pressure of not more than 15 bar.

9. A metathesis catalyst to be used in the process according to any one of claims 1-8, characterized in that it comprises 0.1-40% of weight of a wolfram compound on a silica carrier, which is a magnesium- or titanium-containing co-gel prepared by means of a co-gelling system, which co-gel is optionally calcinated by heating at 300-800°C for 15 - 20 hours.
10. A catalyst according to claim 9, characterized in that the calcination is performed in the presence of air or of an olefine containing 2-20 carbon atoms at a temperature of 400-450°C.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 91 31 1287

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	CATALYSIS REVIEWS. vol. 3, no. 1, 1969, NEW YORK US pages 37 - 60; G. C. BAILEY: 'OLEFIN DISPROPORTIONATION' * page 42, paragraph 5 * * page 43, paragraph 8 * ---		C07C6/D4 B01J23/30
A,D	EP-A-0 152 112 (PHILLIPS PETROLEUM COMPANY) ---		
A,D	US-A-4 559 320 (REUSSER) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07C B01J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11 MARCH 1992	Examiner J. VAN GEYT
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